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# I. Synthesis of Thiazane Derivatives.

# II. Reactivity of Various Alkyl Bromides With Diphenyl Thiourea.*

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## PART I.

## Synthesis of Thiazane Derivatives.

THE meta-thiazanes are six membered heterocyclic ring compounds consisting of four carbon atoms with a nitrogen and sulphur atom meta to each other.

The following formula illustrates the simplest reduced meta-thiazane ring and its numbering:

$$\overset{1}{S} - \overset{2}{CH_2} - \overset{3}{NH} - \overset{4}{CH_2} - \overset{5}{CH_2} - \overset{6}{CH_2}$$

(*a*) Derivatives of this type were first synthesized by F. Foerster (*1*) by the action of trimethylene dibromide upon thiocarbanilide, which gave 2-phenylimino-3-phenyl-1-3-thiazane.

$$\begin{array}{l} S - C{:}NC_6H_5 - N - C_6H_5 \\ \quad\;\; | \qquad\qquad\qquad\quad | \\ CH_2 - CH_2 - CH_2 \end{array}$$

(*b*) They have been obtained, also, by the interaction of trimethylene dibromide (*2*) or chlorobromide (*3*) with thioamides.

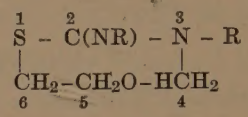
(*c*) And from gamma halogenated amines with carbon disulphide, alkali rhodanides, mustard oils or thioamides (*4*).

(*d*) The loss of water from gamma-oxy-thioureas (*5*) and various syntheses involving the loss of water from thioderivatives (*6, 7, 8*) has resulted in the same type of ring closure.

* From a thesis submitted to the graduate faculty of the University of Kansas in partial fulfillment of the requirements for the degree of doctor of philosophy.

In the chemical laboratory of the University of Kansas such meta-thiazanes have been prepared easily and smoothly from alpha-propanol-alpha-beta-diaryl thioureas, $RNHCSNRCH_2CH_2CH_2OH$. When such compounds are heated with acids, the ring is closed, yielding 2-arylimino-3-aryl-m-thiazanes (*9*), $S\text{-}C(NR)NRCH_2CH_2CH_2$.

The present paper is a study of some interesting derivatives of these thiazanes which contain an hydroxyl group in position 5 and have the general formula:



## EXPERIMENTAL.

### SYNTHESE OF 2-ARYL-IMINO-3-ARYL-5-HYDROXY-1, 3-THIAZANES FROM AMINES, EPICHLORHYDRIN AND MUSTARD OILS.

The general reactions involved in this synthesis are as follows:

Cohn and Friedlander (*12*) have shown that epichlorohydrin adds to primary amines with the formation of a gamma-chloro-beta-hydroxy derivative of a secondary propyl-aryl-amine.

$$\text{I. } RNH_2 + \overset{\overset{O}{\frown}}{CH_2 - CH} - CH_2Cl = RNHCH_2 . CH_2OH - CH_2Cl.$$

Aryl-isothiocyanates (*11*) have been found to unite with the substituted amine, forming a thiourea.

$$\text{II. } RNHCSN(R)CH_2CHOHCH_2Cl.$$

which is too unstable to be isolated, but with loss of hydrogen chloride goes over to the 5-hydroxy thiazane.

In practice the following general procedure has been found advisable. Alcoholic solutions of the amine and epichlorohydrin are allowed to stand in a covered beaker for twelve hours or more and the mustard oil dissolved in alcohol is then added. The solution on slow evaporation in the air gradually deposited crystals mixed with a semi-solid residue. This mass is extracted at water-bath temperature with dilute hydrochloric acid (1:5), the extraction being repeated with fresh acid if necessary.

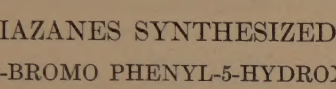
The acid solution is cooled, allowed to stand over night and filtered from the insoluble residue.

The clear filtrate is now poured into an excess of ice-cold dilute ammonium hydroxide, and the solid thiazane, after drying, is purified by repeated crystallizations from alcohol and from benzene.

The product, insoluble in acid, was found to consist of substituted thioureas from the mustard oil and unchanged amine and unidentified oily residues.

## THIAZANES SYNTHESIZED.

### 2-PHENYL IMINO-3-p-BROMO PHENYL-5-HYDROXY-1, 3-THIAZANE.



*Materials Used.*

34.4 g. p-bromo aniline.
18.5 g. epichlorohydrin.
27 g. phenyl mustard oil.
100cc. alcohol.

The yield of thiazane was 20 grams, which melted after recrystallization from alcohol or benzene at 177°.

Analyses: Calculated for $C_{16}H_{15}ON_2SBr$; N, 7.71.

Found: N, 7.52%, 7.36.

The hydrochloride had a melting point of 191°.

From the acid-insoluble portion in this preparation was isolated 4-bromo-diphenyl-thiourea.

### 2-p-TOLYL IMINO-3-BETA-NAPHTHYL-5-HYDROXY-1, 3-THIAZANE.

*Materials Used.*

15 g. beta-naphthyl amine.
10 g. epichlorohydrin.
12 g. p-tolyl isothiocyanate.
200 cc. alcohol.

The yield was six grams, with a melting point of 152° when crystallized from alcohol.

Analyses: Calculated for $C_{21}H_{20}ON_2S$; N, 8.05.

Found: N, 8.23.

### 2-p-TOLYL IMINO-3-PHENYL-5-HYDROXY-1, 3-THIAZANE.

*Materials Used.*

50 g. aniline.
50 g. epichlorohydrin.
80 g. p-tolyl isothiocyanate.
100 cc. alcohol.

The thiazane which was obtained in 44% yield was purified from alcohol and had a melting point of 139°.

Analyses: Calculated for $C_{17}H_{18}ON_2S$; N, 9.40.

Found: N, 9.43, 9.21.

### 2-o-TOLYL IMINO-3-o-TOLYL-5-HYDROXY-1, 3-THIAZANE.

*Materials Used.*

107 g. o-toluidine.
92.5 g. epichlorohydrin.
149 g. o-tolyl mustard oil.
250 cc. alcohol.

The thiazane from alcohol had a melting point of 139° to 140° and only 22 grams of the pure base were isolated.

Analyses: Calculated for $C_{18}H_{20}ON_2S$; N, 8.98%.

Found: N, 9.21%, 8.87%.

### SYNTHESES OF 2-ARYL IMINO-3-ARYL-5-HYDROXY-1, 3-THIAZANES FROM DI-SUBSTITUTED THIOUREAS AND EPICHLOROHYDRIN.

In previous papers (*14*) it was shown that thiocarbanilide and epichlorohydrin gave the same diphenyl hydroxy thiazane that could be formed from aniline, epichlorohydrin and phenyl isothiocyanate. Further work has indicated that the mechanism of the reaction between the thiourea and epichlorohydrin is as follows:

First, a thioether is formed:

$$\text{I.}\quad RNHCSNHR + ClCH_2\overset{\overset{\Big\lceil O \Big\rceil}{|}}{CH}-CH_2 = RN-\overset{\overset{RNH}{|}}{C}-S-CH_2\overset{\overset{\Big\lceil O \Big\rceil}{|}}{CH}-CH_2 = A.$$

Second, the ethylene oxide grouping can add to the RNH group, thus closing the ring and yielding the thiazane or the thioether can react with water and give an oxyurea RNHCONHR and a mercaptan:

$$A + H_2O = RNHCONHR + HSCH_2\overset{\overset{\Big\lceil O \Big\rceil}{|}}{CH}-CH_2 \text{ or } HSCH_2CHOH.CH_2OH$$

The evidence for the above series of reactions is the fact that thiazanes identical with those previously obtained and oxyureas were isolated and positive proof of the formation of a mercaptan obtained. The observation that thioureas are disulphurized by boiling in aqueous solution with ethylene chlorohydrin would seem to confirm the above explanation. The following case will illustrate the general experimental method:

### 2-PHENYL IMINO-3-PHENYL-5-HYDROXY-1, 3-THIAZANE.

*Materials Used.*

50 gr. thiocarbanilide.
25 g. epichlorohydrin.
100 cc. alcohol.

The mixture was heated for eight hours on the water bath. The

alcohol was then distilled off. From the residue in the flask was isolated diphenyl urea, m. p. 234-5° and the thiazane (*19*), with a melting point of 175°.

Analyses: Calculated for $C_{16}H_{16}ON_2S$; N, 9.86.

Found: N, 9.82, 9.95.

### 2-P-TOLYL IMINO-3-P-TOLYL-5-HYDROXY-1, 3-THIAZANE.

*Materials Used.*

30 g. di-p-tolyl thiourea.
21 g. epichlorohydrin.
50 cc. alcohol.

The mixture was heated for two hours and then extracted with dilute hydrochloric acid to remove the base. The purified thiazane weighed 12 grams and melted at 142-142.5°.

Analyses: Calculated for $C_{18}H_{20}O_2N_2S$; N, 8.98.

Found: 8.77, 8.76.

The residue, insoluble in acid, was di-p-tolyl urea.

### 2-o-TOLYL IMINO-3-o-TOLYL-5-HYDROXY-1, 3-THIAZANE.

*Materials Used.*

60 g. di-o-tolyl thiourea.
42 g. epichlorhydrin.
100 cc. alcohol.

The mixture was heated until everything went into solution. From the reaction product was isolated di-o-tolyl urea and the thiazane, 19 gms. This, after recrystallization from alcohol, melted at 139-140°.

Analyses: Calculated for $C_{18}H_{20}ON_2S$; N, 8.98.

Found: N, 9.21, 9.16.

### DI-m-XYLYL IMINO-3-m-XYLYL-5-HYDROXY-1, 3-THIAZANE.

Epichlorohydrin and the di-xylyl thiourea gave the usual products, di-xylyl urea and the thiazane which after purification from alcohol melted at 146°.

Analyses: Calculated for $C_{20}H_{24}ON_2S$; N, 8.24.

Found: N, 8.24.

## REACTIONS OF THE 5-HYDROXY-THIAZANES.

### *1. Oxalic Acid.*

Equal amounts of dehydrated oxalic acid and di-p-tolyl-hydroxy-thiazane were heated at 140° for an hour with the hope that a mole of water might be split off, leaving an unsaturated ring compound. No reaction occurred and the thiazane was recovered unchanged.

*2. Hydrochloric Acid.*

The thiazane was unaffected on boiling for eight hours with hydrochloric acid (1:1).

*3. Methyl Iodide.*

No definite products were isolated when the diphenyl thiazane was allowed to stand with or heated at its boiling point with methyl iodide.

*4. Oxidation of the Diphenyl-Hydroxy-Thiazane.*

The thiazane (26 g.) was dissolved in 100 cc. glacial acetic acid, diluted with 200 cc. water. To this a solution of potassium permanganate was slowly added. The permanganate was reduced, but the only definite product isolated was a little unchanged thiazane.

It was thought that the secondary alcohol group might be oxidized to a keto grouping, but instead the ring is evidently disrupted. An effort was made to synthesize such a keto compound $S\text{–}C{=}(NR)\text{–}NR\text{–}CH_2COCH_2$ as follows:

## ACTION OF ALPHA, GAMMA DICHLORO ACETONE ON THIOCARBANILIDE.

Thiocarbanilide (45 g.) and the dichloroacetone (25.4 g) were dissolved in 550 cc. of dry acetone and the mixture allowed to stand in a stoppered flask. After four days wartlike growths of light brown crystals began to appear. In the course of 12 days some 50 g. of the salt had separated from the solution.

## STUDY OF THE HYDROCHLORIDE.

Some of the crystalline material from the foregoing reaction was pulverized and kept over the week end in a desiccator containing $H_2SO_4$, connected with suction, before weighing out samples for analyses and study of properties.

## SOLUBILITY.

The solubility of this material in various solvents was observed. With water it gave an acid solution and a curdy-white residue. Alcohol readily dissolved it. In chloroform it first dissolved, but very quickly a chalk-white precipitate formed. It was sparingly or slowly soluble in benzene, toluene, petroleum ether, and ether. Acetone dissolved it more readily.

## MELTING POINT OF SALT.

The melting point of the material dried in the desiccator was: darkened, 155°; blackened, 185°; fused, 187°. Melting point of some

of the material precipitated from chloroform solution, after washing with chloroform and drying, was: darkened, about 150°; blackened, about 180°; fused, 186-187°. A sample of the original growth of crystals, after washing with acetone, crystallizing from alcohol, again washing with acetone, gave as melting point: darkened, 160-170°; fused, 188-190.5°. Some of the material dried in the desiccator, crystallized from benzene, washed with acetone, gave as melting point: darkened, 185-190°; fused, 195-196°.

This data on melting points, the results of solubility tests, and the method of formation, with the following analysis, point to these wartlike deposits being a hydrochloride of a base.

## AMOUNT OF HYDROGEN CHLORIDE IN THE HYDROCHLORIDE.

Some of this hydrochloride was suspended in water and its acidity determined by running in a measured amount of NaOH solution and titrating back with $H_2SO_4$ solution. With methyl red as indicator: found 12.22% and 11.62% HCl. With phenolphthalein as indicator: found 12.16% and 12.35% HCl. Average of all determinations is 12.21% HCl.

## TOTAL CHLORINE IN THE HYDROCHLORIDE.

The amount of chlorine in the hydrochloride was determined by the liquid ammonia method (*15*). The first set of analyses gave 23.56% and 23% and 29% of Cl. The second set of determinations gave 20.40% and 20.33% of Cl. It was thought that the variation in analyses of the two sets of samples might be due to variation in the period of drying.

## HYDROCHLORIDE CONTINUES TO LOSE WEIGHT ON HEATING.

A weighing bottle filled with the hydrochloride was placed in a drying oven at 50-60°. At the end of 27 days the sample was still losing weight.

| Day of experiment. | Weight of bottle and sample, grams. | Day of experiment. | Weight of bottle and sample, grams. |
|---|---|---|---|
| 1 | 14.0402 | 22 | 12.3524 |
| 3 | 13.0975 | 23 | 12.3436 |
| 7 | 12.8451 | 24 | 12.3367 |
| 9 | 12.8251 | 25 | 12.3339 |
| 16 | 12.5149 | 27 | 12.3271 |
| 20 | 12.3784 | 28 | 12.3240 |
| 21 | 12.3594 | | |

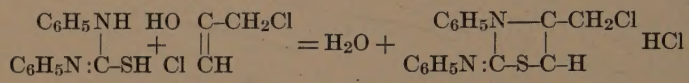
## NITROGEN IN THE HYDROCHLORIDE.

The amount of nitrogen in the hydrochloride was determined by the Gunning method: found 8.17% and 8.16%.

## STUDY OF THE BASE.

The hydrochloride was dissolved in dilute hydrochloric acid, filtered from a little insoluble portion and the filtrate poured into an ice-cold ammonium hydroxide solution. A white precipitate was obtained which was purified by repeated crystallization from benzene and acetone. The resulting base contained chlorine and melted at 152°.

The results of the following analyses show that the original compound contains two atoms of chlorine, one in the form of hydrogen chloride and the other rather loosely bound in the molecule. The most probable explanation is that the dichloroacetone reacts with the thiocarbanilide in the enol form yielding 2-phenyl imino-3-phenyl-4-chloro methyl-thiazolin.



Analyses: Calculated for the salt $C_{16}H_{13}N_2SCl$, HCl:
$N = 8.31$; $HCl = 10.83$; $Cl_2 = 21.07$.
Found: $N = 8.17$; $HCl = 12.21$; $Cl_2 = 20.40$;
8.16. 20.33.

Calculated for the free base: $C_{16}H_{13}N_2SCl$; $N = 9.32$. Found: 9.20.

Confirmatory evidence for such a thiazol synthesis was found in the work of Traumann (*16*), who obtained 2-phenyl imino-3-phenyl-4-methyl thiazolin by the action of monochloroacetone upon thiocarbanilide.

## SUMMARY.

1. A number of 2-aryl imino-3-aryl-5-hydroxy-1, 3-thiazanes have been made from aryl amines, epichlorohydrin and aryl mustard oils.

3. It has been shown that epichlorohydrin will disulphurize thioureas, converting them into the corresponding oxygen ureas.

4. The action of various reagents upon the hydroxy thiazane has been studied.

5. Dichloroacetone was found to give, with diphenyl thiourea, a thiazolin.

# PART II.

## Reactivity of Various Alkyl Bromides with Diphenyl Thiourea.

### PRELIMINARY NOTICE.

IN the hope that light might be thrown on the nature of the reaction between thiocarbanilide and dichloracetone, a study was made of the speed of reactivity of various alkyl bromides with thiocarbanilide. This was done to determine, if possible, which type of alkyl bromide reacted most readily with the –SH group in one of the tautomeric forms of diphenylthiourea.

Earlier work (*17*), as well as more recent investigations in this laboratory (*18*), has shown that a characteristic reaction of substituted thioureas is their ability to add directly alkyl halides yielding thioethers according to the type reaction.

$$R\ NHCSNHR + RX = R\ NHC(SR)NR.HX$$

From the hydrogen halide salts thus formed, the action of alkalies sets free the thiourea ethers, with the formation of an alkali halide. This alkali halide may be extracted from the other products with water. The measure of the amount of halide in the aqueous solution should give a measure of the amount of thiourea and alkyl halide which reacted.

### METHOD OF PROCEDURE.

The reactions were allowed to take place in a three-necked flask. In the center neck was inserted a water condenser, in the top of which was inserted a small-bore tube to serve as an air condenser. In a second neck was inserted a short-stemmed thermometer, the bulb of which was always kept below the surface of any solution in the flask. In the third neck was inserted a 10 cc. pipette, the inner end dipping into any solution in the flask, the outer end being closed with a short rubber tube and clamp. All insertions were made through tight-fitting corks.

All the reactions were carried out in acetone solution. The calculated weight of thiocarbanilide was put in the flask. About three-fourths of the proper amount of acetone was added. The connections were adjusted and the flask immersed in a water bath. The temperature of this bath was kept at 65-70°. When the solution began to boil, 5 cc. of the alkyl bromide in about half of the remainder

of the acetone was carefully poured in through the water condenser and washed down with the balance of the acetone.

The proportions of the three components of the reaction mixture were 2,000 g. acetone: 1 mol of thiocarbanilide: 1 mol of alkyl halide. In each case 5 cc. of the alkyl halide was used. The densities of the alkyl halides necessary for the calculations were taken from Beilstein. The weight of each alkyl hadile being fixed by the product of its density by the volume, 5 cc., the amounts of acetone and thiocarbanilide were calculated to make the right proportions.

From time to time 10 cc. portions of the boiling solution were drawn out and run into flasks containing 10 cc. of saturated sodium bicarbonate solution and 10 cc. of water. After thorough shaking, precipitated material was removed by filtration and washed on the filter until free from halides, using sufficient wash water to make filtrate and washings 100 cc.

Determinations of the halogen in these filtrates was made by the Volhard method.

## RESULTS.

The net results of these reactions between alkyl bromides and thiocarbanilide in acetone solution are shown in the following table, all time being measured from the beginning of the reaction involved:

| *Bromide.* | *Time.* | *Per cent reacted.* | *Remarks.* |
|---|---|---|---|
| Ethyl | 2 hrs. | 9.62 | At end of 3 hrs. 10 min. 12.48 per cent reacted; equilibrium not reached. |
| N-propyl | 2 hrs. | 12.15 | At end of 2 hrs. 30 min. 12.48 per cent reacted; equilibrium not reached. |
| Iso-propyl | 2 hrs. | 3.01 | This was equilibrium; reached by end of 10 min. |
| N-butyl | 2 hrs. | 5.72 | At end of 3 hrs., 7.82 per cent reacted; equilibrium not reached. |
| Iso-butyl | 1½ hrs. | 5.00+ | Equilibrium. |
| Sec-butyl | 1 hr. | 1.80− | Equilibrium. |
| Ter-butyl | ½ hr. | 68.29 | Maximum per cent reacted commenced to decline. |

## SUMMARY.

Within the limits of this work, one may arrange these bromides as to relative reactivity with thiocarbanilide in acetone solution in this order:

1. Ter-butyl.
2. N-propyl.
3. Ethyl.
4. N-butyl.
5. Iso-butyl.
6. Iso-propyl.
7. Sec-butyl.

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